Waste fatty acid addition to black liquor to decrease tall oil soap solubility and increase skimming efficiency in kraft mills pulping mountain pine beetle-infested wood

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Abstract

Means to economically increase soap recovery by increasing the fatty acid/resin acid ratio of the product tall oil were investigated. Lab tests showed that the addition of tall oil fatty acids, or waste fatty acids from canola processing, could decrease tall oil soap solubility and potentially increase soap skimming efficiency in the affected mills. Analyses indicated that adding waste fatty acids could be economical at fatty acid/resin acid ratios of up to 2.5, even when the recovered tall oil is simply burned in the mill's lime kiln, if natural gas and oil prices were high. Full-scale mill trials subsequently run over a 4-day period confirmed that waste fatty acid addition decreased tall oil soap solubility, increased tall oil soap skimming efficiency, and produced a higher-quality soap that was readily processed in the mill's tall oil plant.

Keywords: mountain pine beetle, lodgepole pine, Kraft mills, wood extractives, resin acids, fatty acids, tall oil soap, soap solubility, acid number

Résumé

Des méthodes visant à augmenter de façon économique la récupération du savon en augmentant le rapport acide gras/acide résinique du produit tallöl ont fait l'objet d'une étude. Des essais de laboratoire ont démontré que l'ajout d'acides gras de résine liquide, ou de déchets d'acides gras provenant du traitement du canola pourrait réduire la solubilité du tallöl saponifié et, possiblement, augmenter l'efficacité de la récupération de savon dans les usines touchées. Des analyses ont indiqué que l'ajout de déchets d'acides gras pourrait s'avérer économique à des ratios allant jusqu'à 2,5 d'acide gras/acide résinique, même lorsque le tallöl récupéré est simplement brûlé dans le four à chaux rotatif de la scierie, si les prix du gaz naturel et du pétrole étaient élevés. Des essais à échelle réelle ont par la suite été effectués à la scierie au cours d'une période de quatre jours. Les essais ont confirmé que l'ajout de déchets d'acides gras réduisait la solubilité du tallöl saponifié, augmentait l'efficacité de la récupération du tallöl saponifié et produisait un savon de plus grande qualité qui était facilement traité à l'usine de tallöl de la scierie.

Mots clés: dendroctone du pin ponderosa, pin tordu latifolié, fabriques de pâte kraft, produits d'extraction du bois, acides résiniques, tallöl saponifié, solubilité du savon, indice d'acidité

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1. INTRODUCTION

Kraft pulping of softwoods converts the free resin and fatty acids and a large percentage of the triglycerides in wood into their sodium salts or *soaps*. Associated with the salts are neutral or unsaponifiable compounds, such as sterols. The salts and unsaponifiable compounds separate from the spent cooking liquor as *black liquor soap*. Wood species, dissolved solids content, and the residual effective alkalinity ($NaOH + \frac{1}{2}Na_2S$) in the black liquor can influence this separation and soap solubility (Uloth et al. 1987; Foran 1992).

The recovered soap is either burnt in the recovery boiler or converted into a blend of fatty and resin acids and neutrals, known as *crude tall oil*, through acidulation in a tall oil plant. About 12 kraft mills in Canada process recovered soap to produce 75,000 tonnes of crude tall oil (CTO) per year (Norman 1982). Although Canadian tall oil is generally of much lower quality than that from southern US kraft mills (Norman 1982) and is often difficult to market, tall oil soap should be recovered to minimise its adverse affects on evaporator and concentrator scaling, black liquor viscosity and combustibility, carryover and recovery boiler plugging, and recovery boiler heat load, etc. (Uloth and Wong 1986; Uloth et al. 2007). In addition, tall oil has a higher heating value—as high as 37.9 MJ/kg of dry solids (16,300 BTU/lb)—and many mills now burn tall oil in their lime kilns to displace a substantial portion of their purchased fossil fuel (Young 1989). With natural gas selling for around $8 Canadian/GJ, the fuel value of tall oil is close to $300/tonne, even before considering the emission reduction credits for burning a renewable fuel.

Recent soap solubility tests and black liquor analyses, using black liquor and soap samples from four BC mills and one Alberta mill pulping very little beetle-killed wood, indicate that tall oil production at mills pulping mountain pine beetle-infested wood could drop substantially due to higher soap solubility in black liquor, a reduced tendency for the soap to "float" off in storage tanks and skimmers, and lower soap acid numbers (Uloth et al. 2007). Tests showed that the minimum soap solubility in mills pulping a large percentage of grey-stage beetle-infested wood has increased from 6.0–8.5 kg of soap per tonne of dry black liquor solids (kg/tDBLS) to 10.2–12.7 kg/tDBLS.

The change in soap solubility and a reduced tendency to float to the surface of the black liquors is largely a result of changes in the acid number of the product soap and the fatty acid (FA) and resin acid (RA) content of the wood, resulting from beetle attack and subsequent fungal infestation. The fatty acid/resin acid (FA/RA) ratio in tall oil produced from soap skimmed in the mills pulping beetle-infested wood has dropped from 1.49–1.86 to 0.72–1.28 kg/tDBLS. This has shifted higher both the soap solubility minimum and the black liquor solids concentration at which soap solubility is minimised. The solids concentrations at which soap solubility is minimised are now consistently in the 35%-49% solids range. In the 17%–32% solids range, where most BC mills try to skim soap, soap solubility increased significantly and now generally ranges from 10.5 to 23 kg/tDBLS. The tall oil soap concentrations in weak black liquor samples from these mills ranged from 11.6 to 32.6 kg/tDBLS and, in many cases, did not greatly exceed the solubility limit in the 17%–32% solids concentration range. Soap could, however, be expected to precipitate at higher solids concentrations, aggravating evaporator and concentrator scaling problems and accumulating in strong liquor storage tanks, where it could cause further operating problems and lead to unstable recovery boiler operation (Uloth et al. 2007).

Observations also indicated that instead of forming a distinctive soap layer on top of the black liquor, soap can form a sludge that sinks to the bottom of storage vessels when the FA/RA ratio drops below about 0.9 (Uloth et al. 2007). The tendency of soap to sink when the FA/RA ratio drops below 0.9 was hypothesised to be due to higher soap density (Pearl et al. 1976). Trials on the evaporator soap skimmer at an Interior BC mill (Mill D in Uloth and Wong 1986) pulping a

large percentage of grey-stage beetle-killed wood recently confirmed very poor skimming efficiencies. Only 13%–38% of the total soap in the feed liquor was skimmed for a low acid number (114–118) and low FA/RA (0.73–0.83) ratio soap (Uloth and Guy 2008). In addition, there were extended periods over the two days of trials when soap skimming stopped completely and the soap levels in the "skimmed" liquor were equal to or higher than those in the feed liquor (Uloth and Guy 2008).

As air addition was ineffective in increasing the tall oil soap skimming efficiency, other methods were investigated. Because the change in soap fatty acid content was largely responsible for the changes in soap solubility and recovery efficiency (Uloth et al. 1987, 2007), the possibility of adding waste fatty acids from the processing of vegetable oils was examined.

The kraft mills in the BC Interior used to produce about 40,000 tonnes of tall oil per year, worth about $12 million as a fuel when natural gas sells for about $8/GJ. Soap recovery and tall oil production at BC Interior mills has fallen by 30%–40% in recent years due to the pulping of high proportions of grey-stage beetle-attacked wood, so there is a significant financial incentive to improve tall oil soap recovery in mills pulping beetle-attacked wood. To determine if the addition of waste fatty acids from vegetable oil processing might decrease tall oil soap solubility (Uloth et al. 2007), a series of laboratory tests was conducted using black liquor and tall oil soap samples from Mill E, and both tall oil fatty acids and a number of waste by-products from different vegetable oil processing plants. Those tests indicated that waste fatty acids could be used to decrease tall oil soap solubility and potentially increase tall oil soap recovery, so a mill trial was subsequently arranged.

2. MATERIALS AND METHODS

2.1 Laboratory Soap Solubility Tests

2.1.1 Determing the tall oil soap solubility curve

Tall oil soap solubility, as a function of black liquor solids content, was measured using black liquor and tall oil soap samples from one BC kraft mill (Uloth et al. 2007) that pulped a very high percentage of grey-stage lodgepole pine chips. The mill had reported difficulties in recovering tall oil soap and large variations in the fired black liquor heating value that correlated to high extractives concentrations in the fired liquor. In addition, when the mill was able to skim soap, separation rates and throughput in the mill's tall oil plant were extremely poor. Weak (15.3% solids) and strong (61.5% solids) black liquor samples were obtained from the mill. The crude tall oil (CTO) content of each liquor sample was determined using the Saltsman and Kuiken (1959) procedure.

By mixing various proportions of unskimmed weak black liquor and strong black liquor, liquors with solids levels between 15% and 55% were obtained. These samples were mixed, then transferred into 250-mL graduated cylinders, then covered and placed in an oven at 90°C. Samples were allowed to sit undisturbed for 6–7 h, considerably longer than the 10–20 minutes needed for complete phase separation (Uloth et al. 1987; Lentz 1977). The insoluble soap, visible on the surface of each sample, was skimmed. The skimmed liquor was sampled and its crude tall oil (CTO) content was determined using the Saltsman and Kuiken (1959) procedure, and converted to soap content by assuming a 60% yield of CTO from soap (Uloth and Wearing 1988).

2.1.2 Tall oil soap analysis

The mill supplied a large sample of tall oil soap skimmed from the weak black liquor storage tank Using 9 Normal sulphuric acid, a 200 g sample of the soap was heated and acidulated in the laboratory to an end pH of 2.4, then allowed to separate overnight in an oven held at 95°C. Tall

oil separation was observed to be very slow and the ultimate tall oil yield was poor (less than 34% by weight versus a normal 50%–60% by weight). The clean product tall oil was analysed. One portion was used to determine the tall oil acid number (PCTM-1 1996), a measure of the free resin and fatty acids in the tall oil that is widely used to assess quality. A second portion was analysed for resin acids using a wet chemical method (PCTM-17 1996). The results of the acid number and resin acid determinations were then used to estimate the fatty acid content of the product tall oil (PCTM-20 1996) and the fatty acid/resin acid ratio (FA/RA) of the soap.

2.1.3 Effect of fatty acid addition on tall oil soap solubility

Samples of tall oil fatty acids (TOFA) were obtained from MeadWestvaco in Charleston, South Carolina, . the Wilbur-Ellis Company canola processing plant in Saskatoon, and from Archers Daniel Midland plants in Quincy and Decatur, Illinois. The acid number and fatty acid concentrations in these by-product fatty acid samples were determined using the appropriate Pulp Chemicals Association tests (PCTM-12 1996; PCTM-20 1996, respectively). Using the measured tall oil concentration in the strong black liquor, the measured soap composition, and the tall oil fatty acid and waste fatty acid stream analyses, the amount of each additive (on a pure fatty acid basis) required to raise the tall oil FA/RA ratio from the measured 0.81 to 2.0 and 5.0 was calculated. The required amounts of either the tall oil fatty acids or by-product streams were then added to an 800 mL sample of the strong black liquor at 90°C. The sample was mixed well and aliquots were then diluted with hot water to produce 250 mL samples with black liquors solids concentrations ranging from 14% to 50%. The black liquor samples were placed in in an oven at 90°C. After overnight settling, the insoluble soap was skimmed from each sample and the hot "skimmed" liquor was then sampled as described above in section 2.1.1. A distinct soap layer was observed on the surface of each sample and, even when the remaining liquor was cooled to room temperature, no soap was visible near the bottom of the graduated cylinder. The crude tall oil (CTO) content of the skimmed liquor was determined using the Saltsman and Kuiken (1959) procedure. The CTO content of the skimmed liquor was again converted to soap content by assuming a 60% yield of CTO from soap (Uloth and Wearing 1988).

2.1.4 Effect of tall oil soap separation aids on tall oil soap solubility

A sample of Infinity PS4068, a commercial tall oil soap separation aid, was obtained from Hercules in Macon, Georgia. A sample of the strong black liquor from Mill E was diluted to 37% solids and aliquots of the (diluted) separation aid were then added to 250 mL samples of the resulting black liquor to give dosages of 0 (the control test), 2, and 5 ppm by volume. The samples were mixed well, placed in graduated cylinders, and held overnight in an oven at 90°C. The insoluble soap was then skimmed from each sample and the "skimmed" liquor was sampled and analysed as detailed in the second paragraph in section 2.1.1 above.

2.2 Mill Skimmer Trials

Soap skimming efficiency studies, with and without fatty acid addition, were conducted around the evaporator soap skimmer at Mill E in October 2008. Immediately prior to the trials, the soap present in the evaporator soap skimmer, which is located between the #3 and #2 effects, was transferred through the homogenisation tank to a secondary skimmer for storage. Black liquor flow to the skimmer was then initiated 4 days before the trials started.

Two trucks, each containing 24 tonnes of a fatty acid product, were loaded hot at the Wilbur-Ellis canola processing plant in Saskatoon. One product was a fatty acid residue (used in earlier lab tests summarised in Figure 4) that is almost pure free fatty acids (acid number approximately 148). It is a solid at room temperature, but melts around 40°C and was readily dissolved in high weight percentages in a canola/sunflower by-product (the test results are illustrated in Figure 4).

The other by-product was a green, partly processed canola oil by-product similar to the by-product #2 (which had an acid number of 118.5) used in our lab studies. The contents of both trucks were still over 32°C (90°F) on arrival at the mill site. The products were pumped off the trucks simultaneously into the line going to an old defoamer storage tank. The two products were mixed in a tee prior to going into the storage tank, which had a dip-tube fill system with a feed pipe that went almost to the bottom of the tank, which reduced foaming. This method improved mixing and reduced the chances of the products possibly layering in the tank. The storage tank was equipped with a hot water coil that kept the blended product above 60°C throughout the trial. The blended product mixed well and remained liquid throughout the trial.

As earlier skimmer studies (Uloth and Wearing 1988) showed that the use of composite black liquor samples greatly reduced scatter in the experimental data, composite samples of the approximately 31% solids black liquor going to and leaving the soap skimmer were taken over a period approximating the liquor retention time (3 h) in the skimmer. Three grab samples of each were taken hourly and composited for analyses. The solids content of each sample was determined using the TAPPI standard test (T 650 om-89 1995). The tall oil content of each sample was determined using a modification of the Saltsman and Kuiken procedure (Saltsman and Kuiken 1959; PCA024 1977). The crude tall oil (CTO) content of the skimmed liquor was again converted to soap content assuming a 60% yield of CTO from soap (Uloth and Wearing 1988).

Sampling started around the evaporator soap skimmer at 9:20 am on October 14 (2008). At the same time, a sample of the skimmed soap was taken from the soap skimmer. The tall oil content of the soap sample, and the acid number and resin acid content of the extracted tall oil, were determined using two sub-samples of the skimmed soap and the standard Pulp Chemicals Association test procedures (PCTM 7 1996, followed by PCTM-1 1996, or PCTM-7 1996). The acid number and the resin acid content of the extracted tall oil were used to calculate the fatty acid content of the product tall oil (PCTM-20 1996) and the fatty acid/resin acid (FA/RA) ratio for the product soap. The tall oil soap acid number was estimated at 122 and the FA/RA at 0.73. Assuming that the soap content of the feed liquor to the skimmer was 25 kg of soap/tDBLS, the amount of fatty acids required to raise the FA/RA to 1.5 was estimated. At 6:00 pm on October14, we began adding 6.4 tonnes per day of the blended canola fatty acids to the weak black liquor going into the weak black liquor storage tank.

Composite feed and skimmed black liquor samples were taken around the evaporator soap skimmer every 3 h through the first 30 h of the fatty acid addition trials, and for 8 h on October 16 and 17. One 3-h composite sample was taken on October 18 before the fatty acids were turned off. The measured differences in tall oil content between the feed and skimmed black liquor (PCA-24 1977) were used to assess the soap skimming efficiency and the effects of fatty acid addition on tall oil soap skimming efficiency.

2.2.1 Weak black liquor sampling and analysis

Weak black liquor (WBL) samples were taken before adding the canola fatty acids and after starting fatty acid addition on October 14. Weak black liquor samples were also taken on October 15, 16, and 17 while fatty acid additions continued. The WBL-into-storage sample was taken using a valve on the bottom of the sample pot used to manually test for temperature and specific gravity. The line was carefully flushed prior to each sampling. Due to the lack of a good sample point, the black liquor-out-of-WBL-storage samples were taken simply by increasing the flow to the specific gravity test pot and sampling the overflow by tilting a sample bottle up to the edge of the sample pot. Both WBL samples were composites; three 250 mL grabs went into each, usually over 6 h. The solids and tall oil content of each sample were determined (T650 om-89, 1995), and differences in the tall oil content between the WBL-into and -out of the WBL storage tank (PCA-

24 1977) were used to assess the effects of fatty acid addition on the tall oil soap skimming efficiency in the weak liquor storage tank.

2.2.2 Tall oil soap sampling and analysis

Once the fatty acids were turned off, the skimmer was isolated so that the skimmed soap would be stored in the skimmer. Because the skimmer had not been operated for almost three years prior to the trial, the operators had some difficulty in setting it up to continuously overflow the skimmed soap. Samples of soap taken from the top of the skimmer on October 14, 16, and 17 had very similar acid numbers (122.1, 118.1, and 119.2, respectively). The fact that the soap acid number did not change with fatty acid addition indicates only that no soap was being skimmed from the tank. The operators restored black liquor flow at a low but controlled rate on October 21 and started to transfer the skimmed soap to the soap storage tank. Composite samples of the skimmed soap were taken on October 21, 22, and 23. They were sent to our lab in Prince George, where they were acidulated using a standard lab test (Uloth et al. 1994). The rate of tall oil separation and the ultimate tall oil yield were monitored for each sample. Samples of the tall oil produced were then taken to determine the acid number and resin and fatty acid content of the product oil using the standard PCTM test procedures (1996 PCTM Test Procedures 1, 17, and 20, respectively).

2.2.3 Determining soap solubility

Since soluble soap cannot be skimmed, calculations based on insoluble or recoverable soap generally give a better and more consistent measure of the performance of a given soap skimmer than soap recovery calculated using the total soap available (Uloth and Wearing 1988). To estimate the soap solubility in the 31% solids liquor going to the evaporator skimmer, three of the feed liquor samples from each day were heated to 90°C, mixed well, and transferred into 250 mL graduated cylinders that were then covered and placed in an oven at 90°C. After overnight settling, the insoluble soap was skimmed from each sample and the liquor was sampled and analysed as detailed in the second paragraph in section 2.1.1 above.

3. RESULTS AND DISCUSSION

3.1 Laboratory Soap Solubility Tests

3.1.1 Soap analysis

Using 9 Normal sulphuric acid, a 200 g sample of soap skimmed from the weak black liquor storage tank at Mill E was acidulated in the laboratory to an end pH of 2.4. The resulting mixture of tall oil, precipitated lignin, and sodium sulphate brine was allowed to separate overnight in an oven held at 95°C. Tall oil separation was observed to be very slow, and the ultimate tall oil yield after more than 18 h was poor (less than 34% by weight versus a normal 50%–60% by weight). The clean product tall oil was analysed and found to have a very low acid number (111), which could account for the very slow separation rates observed and low yield (Uloth et al. 1994). It contained 25.8% fatty acids, 32.1% resin acids, and 42.1% unsaponifiables. The FA/RA ratio was 0.81, near the lowest value seen in our 2006/07 tests on soap samples from mills pulping beetle-infested wood (Allen and Uloth 2007).

3.1.2 Tall oil fatty acid and waste fatty acid stream analysis

The results of analyses on the tall oil fatty acid sample and six waste stream samples received from two canola or soybean processing plants are summarised below. The prices shown are those quoted by suppliers in late 2007 and early 2008. These quoted prices for the waste stream by-products vary with oil and energy costs, and are likely significantly lower now.

Tall Oil Fatty Acids (TOFA)
Acid number (as received): 195.4 (close to the theoretical 198.6 for 100% fatty acids)
Free Fatty Acid Content: >98%
Resin Acid Content: <2%
Handling characteristics: light brown oil, fluid (almost like water) at room temperature.
Pricing: $0.44–0.50 US per lb. (FOB Charleston, South Carolina)

Wilbur-Ellis Canola By-product Oil #1
Acid number (as received): 75.1
Free Fatty Acid content: approximately 55%–57% (the supplier's analyses)
Handling characteristics: thick like molasses, required considerable heat to flow easily. Some white solids were present.
Pricing: $0.195 Canadian per lb delivered to Quesnel, BC.

Wilbur-Ellis Canola By-product Oil #2
Acid number (as received): 118.5
Free Fatty Acid content: approximately 65%–67% (the supplier's analyses)
Handling characteristics: thick oil, would require some heating in colder weather, but fluid at room temperature. Some solids were visible.
Pricing: $0.355 Canadian per lb delivered to Quesnel, BC.

Wilbur-Ellis Crude Canola Oil
Acid number (as received): 29.8
Free Fatty Acid content: a maximum of 1% (the supplier's analyses)
Handling characteristics: flowed easily and contained few solids.
Pricing: $0.455 Canadian per lb delivered to Quesnel, BC.

Wilbur-Ellis Fatty Acid Residue
Acid number (as received): 147.7
Free Fatty Acid content: 100% of the total fatty acids present
Handling characteristics: light brown paste at room temperature; free-flowing liquid at 40°C.
Pricing: $0.42 Canadian per lb delivered to Quesnel, BC.

Archer Daniels Midland Acidulated Canola/Sunflower Soapstock
Acid number (as received): 83.7
Free Fatty Acid content: 90%–95% of the total fatty acids present
Handling characteristics: dark brown/black, free-flowing liquid at room temperature.
Pricing: $0.40 US per lb (FOB Decatur, Illinois).

Archer Daniels Midland Acidulated Soybean/Coconut Soapstock
Acid number (as received): 87.8
Free Fatty Acid content: 90%–95% of the total fatty acids present
Handling characteristics: light brown, fluid at room temperature. Some solids were visible.

Based on higher acid numbers, higher free fatty acid content, good handling characteristics, and costs, laboratory studies focused on using the tall oil fatty acids, canola by-product oil #2, and the fatty acid residue to decrease the tall oil soap solubility.

3.1.3 Black liquor sample analysis

The weak black liquor sample received from the mill was high in solids (28% versus the 15%–17% expected) and contained very high soap concentrations. Duplicate analyses showed tall oil soap concentrations averaging 118.8 kg of soap/tDBLS, as compared to the 29.3 kg/tDBLS seen in the 2007 weak black liquor (WBL) sample from the same mill. A sample of the liquor was subsequently diluted to about 15% solids and left to stand at room temperature. After overnight settling, a "sinking soap" phase was clearly visible at the bottom of the container (Figure 1). Its presence explains both the high solids and high tall oil content measured for the sample and many of the operating problems observed in the chemical recovery system at the mill. Our earlier studies (Allen and Uloth 2007) indicated that instead of forming a distinctive soap layer on top of the black liquor, soap can form a sludge that sinks to the bottom of storage vessels when the FA/RA acid ratio drops below about 0.9. The low FA/RA ratio (0.81) for soap skimmed at the time the weak liquor was sampled is consistent with the presence of the sinking soap layer and high soap concentrations in the feed to the mill's evaporators.

The very high levels of tall oil in the WBL sample made it impractical to use it in experiments to examine the effect of adding fatty acids. The strong black liquor sample contained 14 kg of soap/tDBLS. Although this was not much above the expected soap solubility limit for the 0.81 FA/RA soap, the fatty acid additions would increase the total soap content so the solubility at higher solids concentrations (28%–50% solids) should be safely exceeded.

Figure 1. Diluted weak black liquor (14.5% solids) received from Mill E clearly shows a light brown "sinking soap" phase at the bottom of the container.

3.1.4 Effect of fatty acid addition on tall oil soap solubility

The tall oil soap solubility curve determined at 90°C for the 0.81 FA/RA soap in the mill's black liquor is illustrated in Figure 2. Soap solubility was minimised at a concentration of 12 kg of soap/tDBLS, or 1.2 wt % soap on dry BLS at a black liquor solids concentration of around 50%. While comparable to the values observed for liquor samples from the same mill in 2007 (Allen and Uloth 2007; Uloth et al. 2007), this is much higher than the minimum soap solubility observed in southern US mills pulping a high percentage of pine: 0.5 wt % on dry BLS at a black liquor solids concentration of around 28%.

Using the measured tall oil soap concentration in the strong black liquor (1.4% on DBLS) and the estimated soap composition (FA/RA = 0.81), the amount of fatty acids required to raise the tall oil soap FA/RA ratio from the measured 0.81 to 2.0 and 5.0 was calculated. The required amounts of either the tall oil fatty acids or canola by-product stream #2 were then added to samples of the mill's strong black liquor at 90°C. The sample was mixed well and aliquots were then diluted with hot water to produce samples with black liquors solids concentrations ranging from 14%–50%. The resulting black liquor samples were placed in graduated cylinders and held in an oven at 90°C. After overnight settling, the insoluble soap was skimmed from each sample and the skimmed black liquor samples were analysed to determine the soap solubility at higher FA/RA ratios. The results of these analyses, together with those using other fatty acid by-products at one black liquor solids concentration, are illustrated in Figures 2, 3, and 4.

As expected, the data summarised in Figures 2 through 4 clearly indicate that the addition of tall oil fatty acids, or waste fatty acids from vegetable oil processing, can decrease tall oil soap solubility and potentially increase soap skimming efficiency in the affected mills. Using the weight of the extracted tall oil or gravimetric analyses, raising the FA/RA to 2.0 by fatty acid addition decreased the minimum soap solubility to around 0.9 wt% soap on DBLS at a black liquor solids concentration of 25%. Although the decrease in the minimum soap solubility was not as great as expected, solubility in the 25%–30% black liquor solids concentration range dropped by at least 25%, indicating that soap skimming in the existing equipment could be significantly improved. Fatty acid addition to raise the FA/RA to 5.0 decreased the minimum soap solubility to around 0.6 wt% on DBLS at a black liquor solids concentration of 25%–33%. The expected increase in tall oil acid number resulting from fatty acid addition would also result in reduced separation time requirements after soap acidulation and greatly increase tall oil plant throughput (see Figure 1 in Uloth et al. 1994).

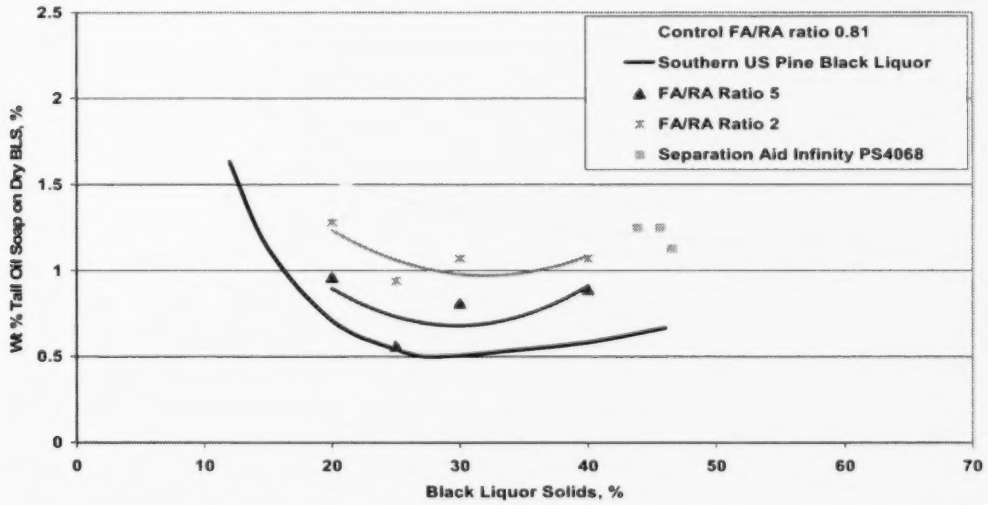

Figure 2. Effect of fatty acid addition using canola by-product #2 on tall oil soap solubility at 90°C in black liquor samples from Mill E.

Note: The tall oil soap in the sample liquors had an initial acid number of 111 and a fatty acid/resin acid (FA/RA) ratio of 0.81. Enough canola fatty acids were added to raise the FA/RA ratio to 2.0 or 5.0. The measured effects of a tall oil soap separation aid, Infinity PS4068, at dosages of 0, 2, and 5 ppm by volume in 45% solids black liquor are also summarised (using the purple square symbols).

The measured reductions in tall oil soap solubility resulting from fatty acid addition and the expected increase in the FA/RA ratio were not as great as would have been predicted from our earlier data for mills with FA/RA ratios between 1.5 and 1.8 (Uloth et al. 1987; Allen and Uloth 2007). In addition, the measured reduction in tall oil soap solubility resulting from fatty acid addition in our laboratory tests (see Figures 2 and 3) was variable.

As illustrated in Figure 3, the measured gravimetric solubilities (the red diamonds) at higher black liquor solids concentrations (>25% solids) were close to those estimated by titration of the extracted tall oil (the solid squares) if we assigned an acid number (115) similar to that of the soap in the original black liquor (111).

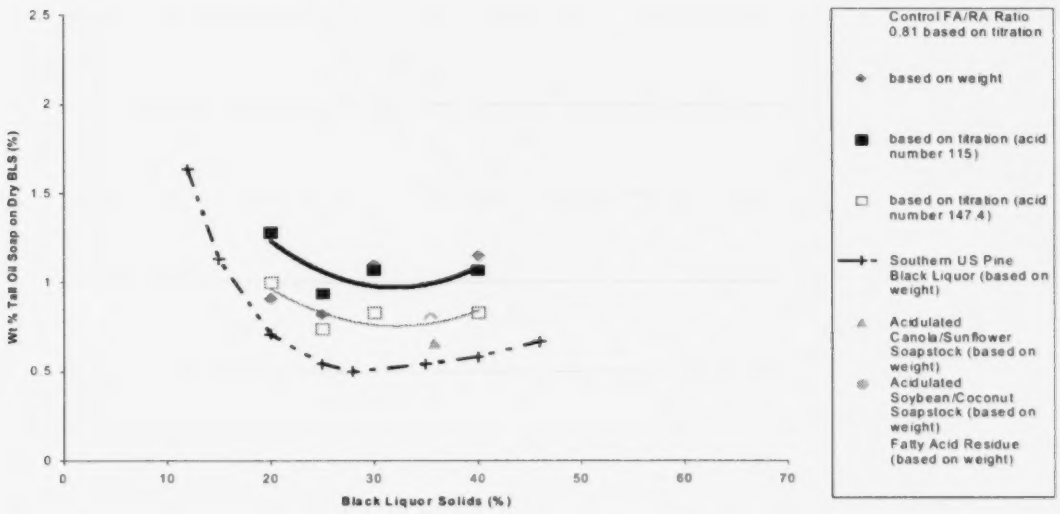

Figure 3. Effect of fatty acid addition using canola by-product #2 and other waste fatty acid streams on tall oil soap solubility at 90°C in black liquor samples from Mill E.

Note: Tall oil soap in the sample liquors had an initial acid number of 111 and a fatty acid/resin acid (FA/RA) ratio of 0.81. Enough waste fatty acids were added in all tests to raise the FA/RA ratio to 2.0. The results from both weighing (the Xs) and titrating the extracted tall oil from the by-product #2 tests are illustrated assuming tall oil acid numbers of 115 (solid squares) and 147 (open squares). Results for other fatty acid by-product streams (the triangles, solid circles, and diamonds) at about a 35% black liquor solids concentration are those from weighing the extracted oil.

The measured gravimetric solubilities at lower black liquor solids concentrations were, however, close to those estimated by titration of the extracted tall oil (the open squares) if we assigned an acid number (147) similar to that expected to result from complete fatty acid incorporation into the soap in the original black liquor. The observed erratic results might be due to variations in soap solubility with changing liquor solids concentrations and inconsistent mixing in the laboratory experiments. We hoped that better mixing in mill scale equipment, and introducing the fatty acids early in the process where soap solubility was very high, would improve the incorporation of the added fatty acids in the soap micelles, further reduce tall oil soap solubility, and increase soap skimming efficiencies. The lab results, however, were encouraging and clearly supported the need for full-scale tests to better quantify the potentially beneficial effects of fatty acid addition on soap skimming efficiency in existing mill equipment. With the co-operation of staff at Mill E, a mill trial was arranged.

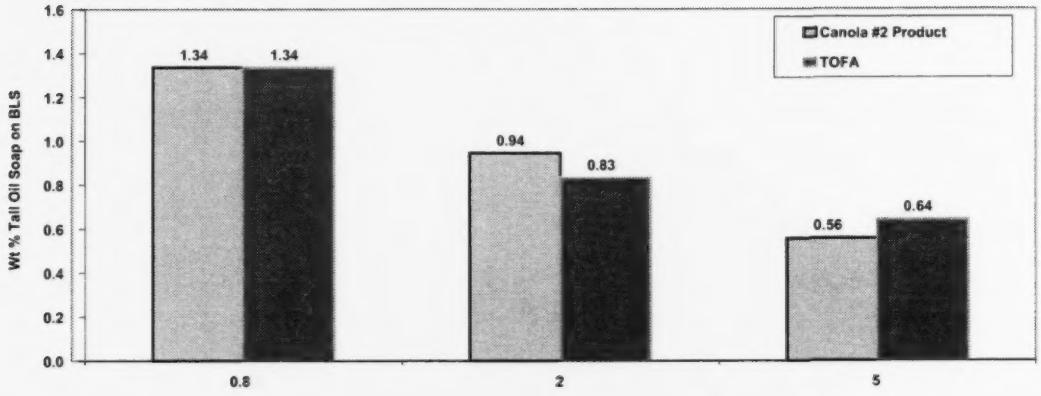

Figure 4. Effect of adding tall oil fatty acids or waste fatty acids from canola processing (By-product #2) on tall oil soap solubility in Mill E's 25% solids black liquor at 90°C.

3.1.5 Effect of tall oil soap separation aids on tall oil soap solubility

We were not able to locate a supplier for the soap separation aid Rezosol 8201 tested in the late 1980s that was found to be effective in increasing tall oil soap skimming efficiencies in several BC kraft mills (Uloth and Wearing 1988). We did get a sample of the tall oil soap separation aid Infinity PS4068, however. It was tested at dosages of 2 and 5 ppm by volume and, as illustrated in Figure 2 (by the purple squares around the 45% black liquor solids concentration), found to have no impact on tall oil soap solubility. Data from earlier mill trials indicated that chemical separation aids (either Rezosol 8201 or a lignosulphonate) tested separately (Uloth and Wearing 1988) never dropped the skimmed liquor soap concentrations below the solubility limit.

3.2 Mill Skimmer Trials

3.2.1 Tall oil soap analyses

Soap sampled from the top of the skimmer at Mill E (as outlined in sections 2.2 and 2.2.2) on October 14 (before adding fatty acids), 16, and 17 (after adding fatty acids) had very similar acid numbers: 122.1, 118.1, and 119.2, respectively. The fact that the soap acid number did not change with fatty acid addition indicates only that no soap was being skimmed from the tank. As summarised in Table 1, these soap samples all had FA/RA ratios between 0.69 and 0.73. On the other hand, a sample of soap skimmed from the 31% solids black liquor feeding the evaporator soap skimmer on October 17 had an acid number of 135.2, very close to the theoretical 137 expected if all of the added canola fatty acids were incorporated in a 120 acid number soap.

Table 1. Tall oil soap characteristics before and after the fatty acid addition trials at Mill E.

Soap Sample	Acid Number	Resin Acids (wt. %)	Fatty Acids (wt.%)	FA/RA Ratio	Ultimate Tall Oil Yield After Lab Acidulation (weight %)	Separation Time Required to Recover 75% of the Ultimate Oil Yield, min.
Soap off top of skimmer on Oct 14	122.1	37.1	26.9	0.73		
Skimmed soap - noon Oct 16	118.1	36.6	25.3	0.69		
Soap off skimmer - Oct 17	119.2					
Soap manually skimmed from "skimmer feed liquor" on Oct 17	135.2					
Lab Acidulation Test Results *						
October 15, 2008 "control"	120.4				48.0	>300
October 21, 2008	131.4	36.6	29.8	1.23	54.2	23
October 22, 2008	128.6	35.2	32.7	1.08	21.1	>300
October 23, 2008	130.7	35.5	32.4	1.10	47.0	85
Oct. 15 soap plus 10% Fatty Acids	137.7				40.3	22
Oct. 15 soap plus 20% Fatty Acids	142.7				57.6	28

*The lab acidulation test procedure is outlined in Uloth et al. 1994. Three grams of Tembind A, a lignosulphonate tall oil separation aid, were added to each 200 g soap sample after acidulation. The ultimate oil yield is the oil yield after 20 hours' separation at 90°C. The time to recover 75% of the ultimate oil yield, $T_{0.75}$, (in minutes) is a measure of the separation rate; shorter separation time indicates faster separation, which should increase tall oil plant throughput.

As summarised in Table 1, samples of the soap skimmed on October 21, 22, and 23, when soap skimmed before and during the fatty acid addition trials was being transferred to the soap storage tank, had acid numbers ranging from 128.6 to 131.4, and FA/RA ratios between 1.08 and 1.23. The higher acid numbers and higher FA/RA ratios confirm that the added fatty acids were incorporated into the soap micelles. The fact that the acid number and FA/RA ratio did not reach the levels expected, if all of the added fatty acids were incorporated into the skimmed soap, suggests that either some of the added fatty acids were lost to the soap separating in the weak liquor storage tank, or that the soap skimmed between October 21 and 23 was a blend of the soap skimmed before and after fatty acid addition.

Note that the higher acid number soap skimmed at the end of the fatty acid addition trials separated more rapidly than the soap skimmed before the trial (see the right-most column in Table 1). Only one of the three soap samples skimmed at the end of the trial produced higher tall oil yields than the October 15 control sample. The effect of fatty acid addition on both acid number and yield was not as dramatic as that obtained when either 10% or 20% fatty acids were blended directly into a 120 acid number soap collected from the skimmer before starting the fatty acid addition tests. Blending the fatty acid residue into the tall oil soap skimmed on October 15 did produce acid numbers that exceeded those calculated using the acid number of the "fatty acid residue," suggesting that it may have contained some triglycerides that were converted to free fatty acids when left overnight in the alkaline soap prior to the lab acidulation test.

Tall oil soap transferred from the skimmer after the fatty acid addition trials was successfully processed in the Hydrodynamic Separator (HDS) tall oil plant at Mill E without needing to use any tall oil separation aids. About 165 tonnes of tall oil were produced when the soap skimmed

over the 4 days prior to the trial and the soap skimmed over the four-day long trial were acidulated. Tall oil production was thus slightly over 20 tonnes per day (tpd) for the whole eight days that the skimmer was in operation. The 20.5 tpd of tall oil production is very close to the plant's design capacity of 24 tpd. Acid numbers of the product tall oil, as analysed at the mill, ranged from 122.4 to 128.5 (assuming 2% moisture), which is in line with the results from laboratory acidulations of the skimmed soap. The FA/RA ratio in the product tall oil ranged from 0.96 to 1.24, which is also in line with our laboratory soap acidulation test results.

3.2.2 Soap removal in the weak black liquor storage tank

The tall oil soap content of samples of weak black liquor (WBL) going into and coming out of, the weak black liquor storage tank was determined before and during the trial. As summarised in Table 2, there were significant reductions in the concentration of soap across the WBL storage tank. Soap removal after adding the fatty acids was significantly greater than that seen before the trial. The soap concentrations in the feed liquor, however, were highly variable and often unrealistically high. As the concentrations of soap in the liquor coming out of WBL storage were consistent with the concentrations typically seen in the 31% solids black liquor going into the soap skimmer (16–21.4 kg/tDBLS), we must conclude that the WBL samples going into the storage tank were not representative for some reason.

Table 2. Weak black liquor characteristics before and during the fatty acid addition trials at Mill E.

Sample Date	WBL into Storage		WBL out of Storage		Soap Skimming Efficiency, % (based on total soap)
	Solids Content wt%	Tall Oil Soap Content, kg/tDBLS	Solids Content wt%	Tall Oil Soap Content kg/tDBLS	
October 14 before starting fatty acid addition	17.9	67.1	18.1	21.1	68.6
October 14 after starting fatty acid addition	18.0	150.4	18.6	11.1	92.6
October 15	15.9	198.0	15.9	19.0	90.4
October 16	19.6	341.3	18.0	21.4	93.7
October 17	18.0	63.0	19.2	16.6	73.7

Note: For the tall oil analyses (PCA 24 1977), the soap acid number was assumed to be 122 before starting fatty acid addition, 128 in the transition period late on October 14, and 135 with fatty acid addition on October 15, 16, and 17.

3.2.3 Tall oil soap solubility tests

After double-checking the analyses for a few black liquor samples from the skimmer efficiency tests, three of the feed liquor samples from each day were mixed well, covered, and sat overnight in an oven at 90°C. The insoluble soap was skimmed from each sample and the still-hot skimmed liquor was then sampled as detailed in section 2.1.1. The solids content and crude tall oil (CTO) content of the skimmed liquors were determined in order to estimate tall oil soap solubility in the skimmer so that skimming efficiency could be calculated based on both the total soap available and the insoluble soap.

Soap solubility in the feed liquors before adding fatty acids ranged between 10.1 and 13.5 kg/tDBLS for four samples analysed, and averaged 11.4 kg/tDBLS for the 31% solids liquor on October 14. This is somewhat lower than the solubility of about 13.5 kg/tDBLS seen in Figure 2 for the 31% solids liquor from Mill E in the October 2007 lab tests. The observed lower solubility

is somewhat surprising considering the lower tall oil FA/RA ratio (0.7 vs 0.81 in October 2007). The lower soap solubility may reflect the higher soap acid number (120 vs 111 in October 2007) and suggests that acid number and FA/RA ratio likely influence tall oil soap solubility.

Soap solubility in three daily composite feed liquor samples taken after fatty acid addition commenced ranged from 6.6 to 10.9 kg/tDBLS, and averaged 8.8 kg/tDBLS. The lower measured soap solubility confirms that fatty acid addition had the desired effect on tall oil soap solubility.

Four of the five skimmed liquor samples taken before starting to add the fatty acids had soap concentrations lower than the laboratory-measured solubility limit. Similarly, 13 of the 14 skimmed black liquor samples taken after fatty acid addition commenced had soap concentrations lower than the laboratory-measured solubility limit. Soap concentrations in several of the skimmed liquors taken near the end of the trial were exceedingly low (4.0–4.7 kg/tDBLS). For this reason, we assumed a soap solubility limit of 5 kg/tDBLS during the baseline tests, and 3.5 kg/tDBLS after starting fatty acid addition. Why such a large percentage of the soap concentrations in the skimmed liquor could be lower than the laboratory-estimated solubility needs further investigation. It cannot be explained by temperature differences because the skimmer operated at close to 200°F (93°C) throughout the trials.

3.2.4 Evaporator soap skimmer test results

The concentrations of soap in skimmed black liquor are shown as a function of the concentration of soap in the feed liquor in Figure 5. The results of extensive testing around the soap skimmer in 1997, prior to the mountain pine beetle infestation, are also illustrated (by the open square symbols) in Figure 5. The diagonal line with the feed concentration equal to that in the skimmed liquor indicates (and is so marked) "No Skimming." Points lying close to the line indicate poor skimming, while points below and further removed from the line are indicative of good soap skimming. One sample taken before adding fatty acids (shown with a blue diamond symbol), lies very close to the "No Skimming" line. Trials on the evaporator soap skimmer at another Interior BC mill (Uloth and Guy 2008) recently confirmed very poor skimming efficiencies for mills processing a high percentage of grey-stage beetle-infested wood. Only 13%–38% of the total soap in the feed liquor was skimmed with a low acid number (114–118), low FA/RA ratio (0.73–0.83) soap. In addition, there were extended periods over the two days of trials at that mill when soap skimming stopped completely and the soap levels in the "skimmed" liquor were equal to or higher than those in the feed liquor. This one data point for the 120 acid number, low FA/RA ratio (0.69–0.73) period of the trial may indicate similar periodic skimming problems at Mill E.

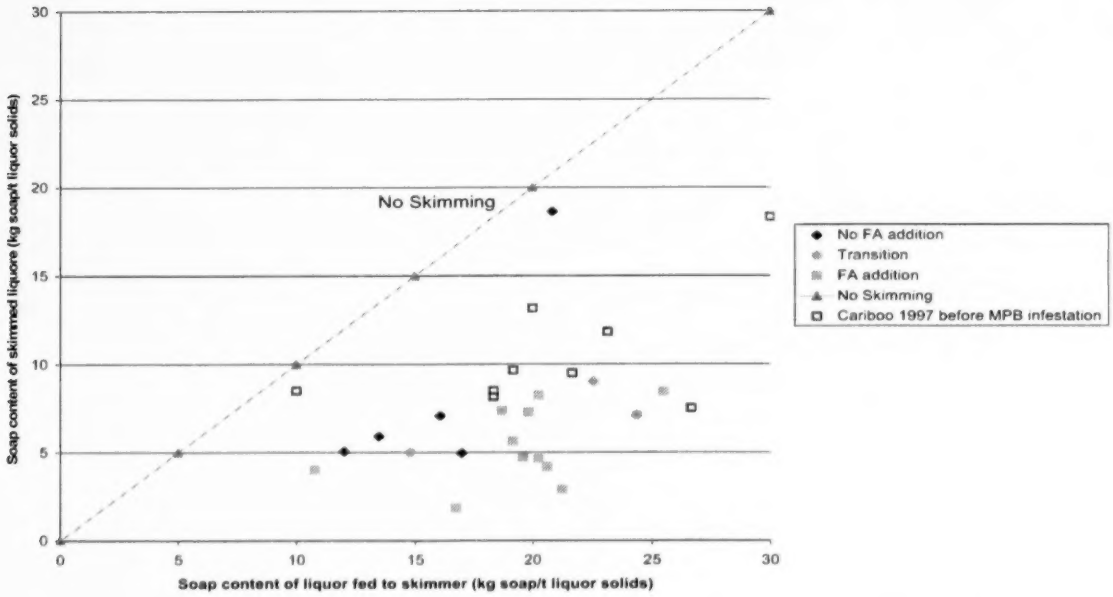

Figure 5. The concentrations of tall oil soap in the liquor fed to and leaving the evaporator soap skimmer at Mill E over four days of testing.

Note: Soap concentrations are those estimated from titrating the extracted tall oil in composite black liquor samples (PCA-24 1977). The tall oil acid number was estimated at 120 before fatty acid addition, 128 in the transition period, and 135 after adding fatty acids.

Most liquor samples taken after starting to add fatty acids showed higher concentrations of soap in the feed liquor, and equal or lower concentrations of soap in the skimmed black liquor, when compared to samples taken before adding fatty acids. This indicates that fatty acid addition improved the tall oil soap skimming efficiency. While soap concentrations were not as high as those seen in the 1997 tests, the soap concentrations in the skimmed liquor were generally lower, again confirming improved skimming efficiencies as a result of fatty acid addition. Figure 6 shows that the tall oil soap skimming efficiency, based on total soap available, increased from 50.2% in the baseline tests to 71.8% with fatty acids added.

The 50% skimming efficiency based on total soap available is very similar to the 53% average found by the mill during the extensive 1997 testing. If the one period of poor skimming is dropped from the baseline data set, on average, still only 60.2% of the total soap was skimmed before starting to add fatty acids.

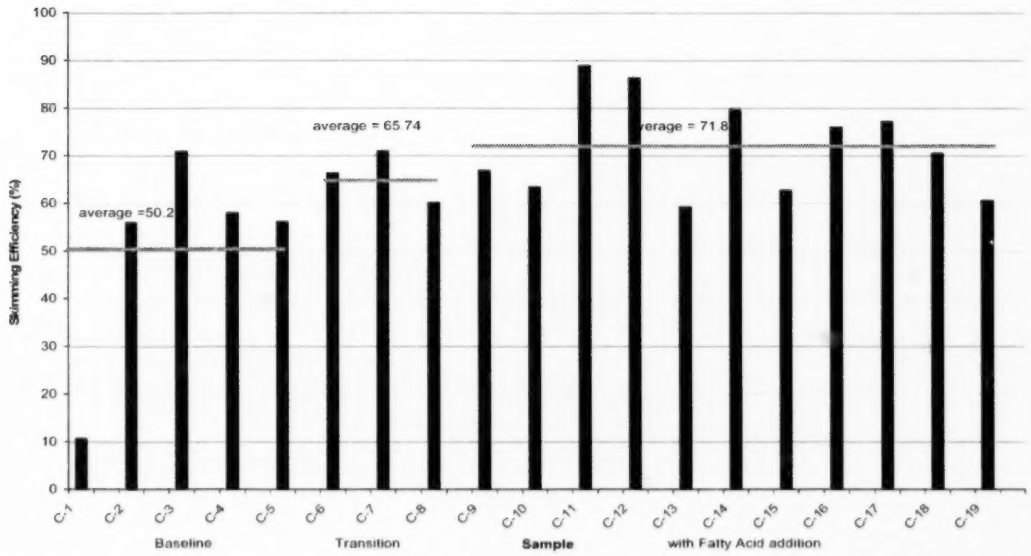

Figure 6. The effect of fatty acid addition on tall oil soap skimming efficiency at Mill E based on total soap in the feed liquor.

Note: Soap concentrations are those estimated from titrating the extracted tall oil in composite black liquor samples (PCA-24 1977). The tall oil acid number was estimated at 120 before fatty acid addition (samples 1-5), 128 in the transition period (samples 6-8), and 135 after adding fatty acids (samples 9-19).

Similarly, Figure 7 shows that the tall oil soap skimming efficiency, based on insoluble soap only, increased from 76.7% in the baseline tests to 87.5% with fatty acids added.

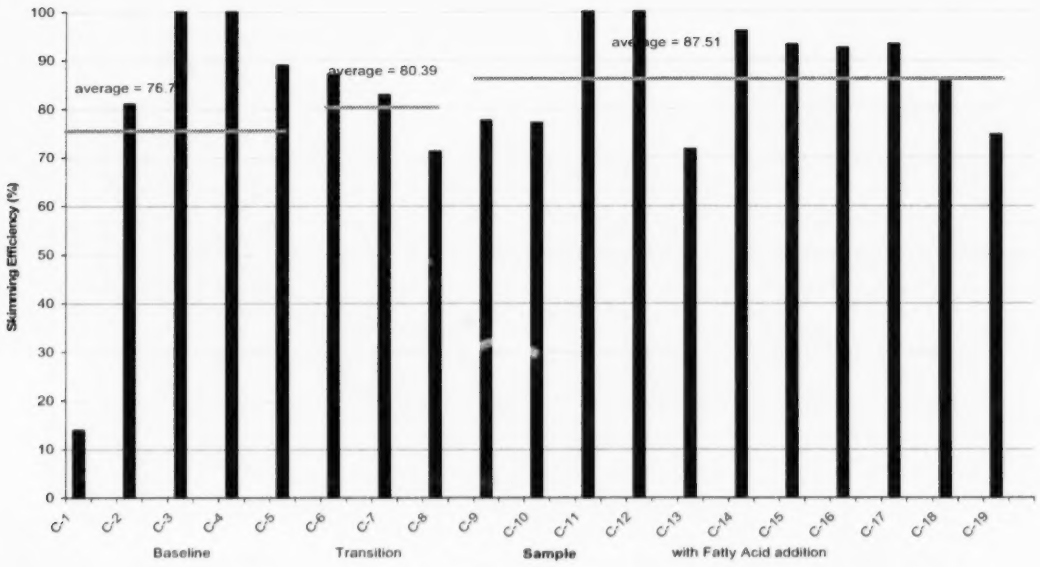

Figure 7. The effect of fatty acid addition on tall oil soap skimming efficiency at Mill E based on insoluble soap in the feed liquor.

Note: Soap concentrations are those estimated from titrating the extracted tall oil in composite black liquor samples (PCA-24 1977). The tall oil acid number was estimated at 120 before fatty acid addition (samples 1-5), 128 in the transition period (samples 6-8), and 135 after adding fatty acids (samples 9-19).

To extract maximum data from the skimming trials, we weighed the extracted tall oil in each laboratory analysis, dissolved it in isopropanol, and then titrated the extracted tall oil for each liquor sample using methanolic potassium hydroxide (PCA-24 1977).

To use the titration results, one must insert an estimated acid number into the denominator of an equation to calculate the weight of tall oil and estimate the weight percent tall oil on dry black liquor solids.

Figure 8 shows the comparison between the percent crude tall oil (CTO) estimated for the baseline and transition samples from weighing the extract and titrating it. For the data shown in Figure 8, the weight of tall oil before adding fatty acids was estimated for the titration, assuming a tall oil acid number of 120 based on the analyses of soap samples taken off the skimmer on October 14, 16, and 17 (see Table 2). The weight of tall oil in the transition period (samples 6 through 8) was estimated in the titration by assuming a tall oil acid number of 128, midway between the 120 and the 135 determined by analysing soap skimmed from the feed liquor on October 17.

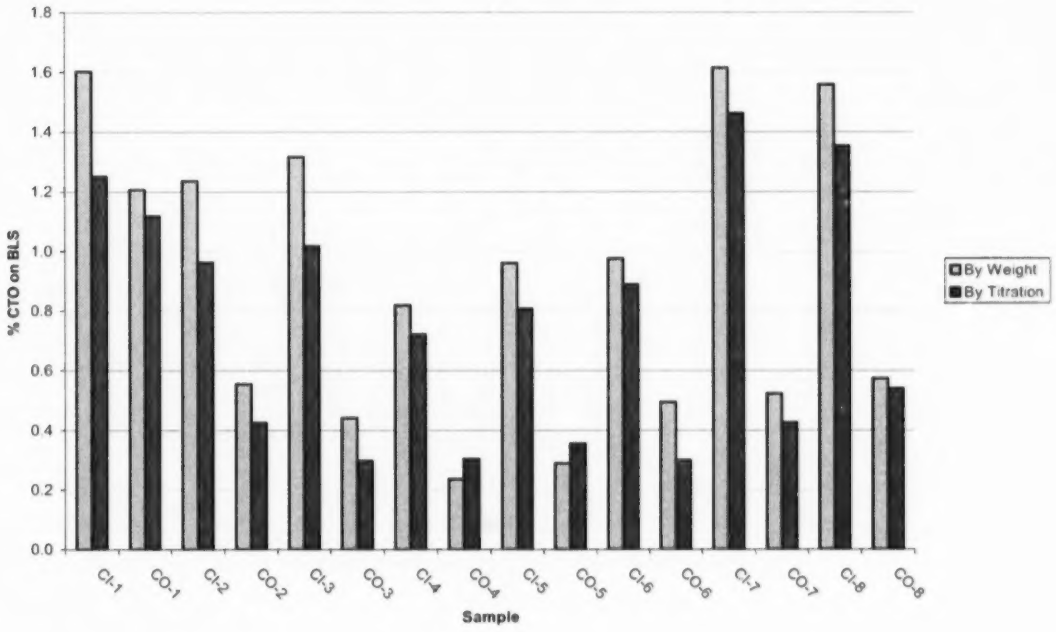

Figure 8. Weight % crude tall oil on dry black liquor solids in the feed and skimmed black liquor samples during the baseline and transition period tests.

Note: CTO weight was determined by both weighing and titrating the extracted tall oil (PCA-24 1977). The titration was converted into a weight estimate assuming a tall oil acid number of 120 before fatty acid addition (samples 1-5), and 128 in the transition period (samples 6-8).

Figure 9 compares the percent CTO estimated from weighing to that by titrating the extract for samples taken more than 12 h after starting to add fatty acids. The weight of tall oil after adding fatty acids was estimated assuming a tall oil acid number of 135, determined by analysing soap skimmed from the feed liquor on October 17. In both Figures 8 and 9, the weight percent soap on DBLS estimated using titration results was consistently lower than those estimated using the gravimetric results, suggesting that the acid numbers used in converting the titrations into a weight of tall oil (120 before fatty acid addition, 128 in the transition period, and 135 after adding fatty acids) may have been high. To adjust the titration-estimated weights to closely match those determined gravimetrically, we would have needed to use an acid number of 95 for samples taken before adding fatty acids, and an acid number of 116 for those taken after adding them.

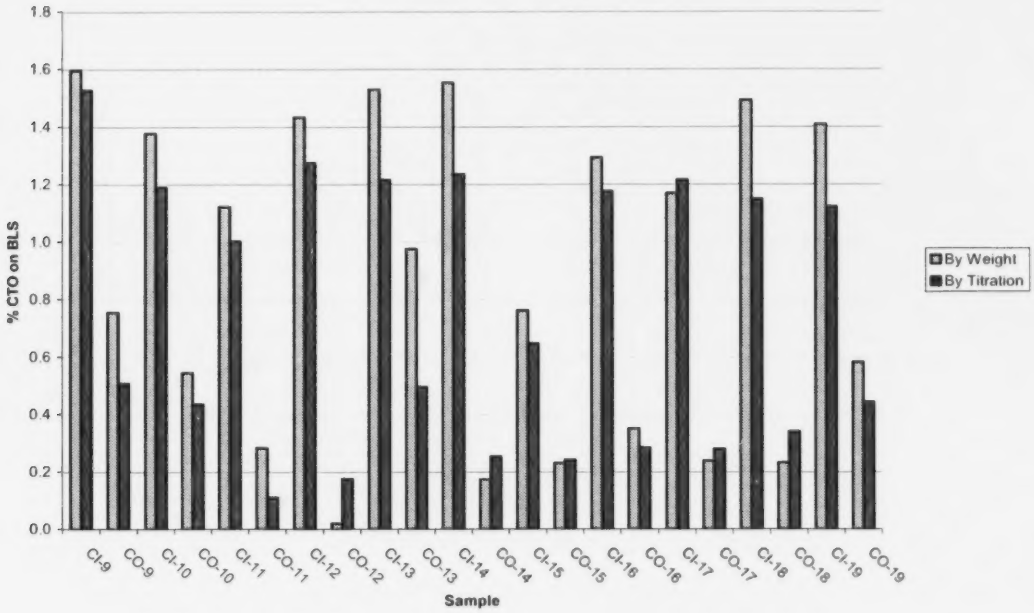

Figure 9. Weight % crude tall oil (CTO) on dry black liquor solids in the feed and skimmed black liquor samples following fatty acid addition to the weak black liquor.

Note: CTO weight was determined by both weighing and titrating the extracted tall oil (PCA-24 1977). The titration was converted into a weight estimate assuming a tall oil acid number of 135 after fatty acid addition.

Changes in soap recovery and skimming efficiency resulting from fatty acid addition were similar whether we used tall oil contents estimated by weighing or by titrating the extracted oil (Table 3). Titration results used in Figures 5–7 give slightly more conservative estimates.

Table 3. Effects of adding fatty acid to tall oil soap concentrations in the feed and skimmed black liquor, and on soap skimming efficiency during mill trials.

			Skimming Efficiency (%)	
	Soap in (kg/t BLS)	Soap Out (kg/t BLS)	Based on Total Soap	Based on Insoluble Soap Only
No Fatty Acid Addition				
Based on Weight	19.8	9.1	57.5	72.8
Based on Titration	15.9	8.3	50.3	76.8
With Fatty Acid Addition				
Based on Weight	22.3	6.6	72.7	85.9
Based on Titration	19.3	5.4	71.9	87.5

3.3 Economic Analyses

The economics of adding waste fatty acids from canola processing to reduce tall oil soap solubility and improve soap recovery were examined based on the mill trial results. Economic sensitivity to the required FA/RA ratio, natural gas prices, fatty acid costs, and other variables were examined. Assumptions and costs used in the analyses are detailed in the *Input* section of the spreadsheet (Table 4). Costs of waste fatty acid streams, together with samples of each, were supplied by Jayson Hodgson at Wilbur-Ellis Company in Saskatoon. Economics were evaluated using the costs for the blended by-product number 2 and fatty acid residue waste streams used in the mill trials. We assumed that we could buy this stream for $0.32 per pound, about 17% lower than the spot price quoted by Wilbur-Ellis, through volume buying on a long-term contract.

Economics were evaluated assuming that the tall oil was simply burned in the mill's lime kiln, displacing purchased natural gas. Costs of converting the recovered soap to tall oil were estimated at $50 per tonne of tall oil. These costs included sulphuric acid, caustic for neutralizing waste acid and dissolving lignin, steam, manpower, and electricity. Effects of reducing soap concentration in the fired liquor on recovery boiler capacity were estimated from the reduction in fired solids only, and did not include soap's higher heating value relative to other black liquor solids. Effects of a potential carbon tax on the economics of using this renewable fuel were also included.

The economic analyses indicate that adding waste fatty acid can be very economical (Table 4). Depending on the costs of natural gas and fatty acids, and the required FA/RA ratio for good soap skimming, net profits of $1.4 to $2.8 million per year are estimated, when all the benefits of improved tall oil soap recovery are considered. It could be economical to add waste fatty acid at FA/RA ratios of up to 1.75—even when considering only the value of burning the recovered tall oil in the mill's lime kiln—when natural gas and oil prices were high (>$9 Canadian/GJ). When pulp production lost due to recovery boiler solids input limitations and greenhouse gas credits are included in the analyses (at $15/tonne in the example shown), waste fatty acid addition can be economical at FA/RA ratios of up to 2.5. The increase in the product tall oil acid number resulting from fatty acid addition, from 120 for the soap skimmed before adding fatty acids (FA/RA = 0.7) to as high as 137 for a FA/RA ratio of 1.5, would greatly increase tall oil plant throughput and the possibility of selling the tall oil to fractionators for even greater profits.

Table 4. Economic analysis of adding waste fatty acids to increase tall oil soap skimming efficiency.

	Sensitivity to the Required FA/RA Ratio				Sensitivity to Natural Gas Price			Sensitivity to Fatty Acid Price		
INPUT										
Required FA/RA ratio	1.00	1.20	1.5	1.75	1.2	1.2	1.2	1.2	1.2	1.2
Natural Gas, $Can/GJ	$9.00	$9.00	$9.00	$9.00	$7.00	$9.00	$11.00	$9.00	$9.00	$9.00
Mill Size, pulp production, tonnes per day	950	950	950	950	950	950	950	950	950	950
Tonne BL Solids / Tonne Pulp	1.95	1.95	1.95	1.95	1.95	1.95	1.95	1.95	1.95	1.95
Fatty acid costs, $/lb	$0.32	$0.32	$0.32	$0.32	$0.32	$0.32	$0.32	$0.30	$0.40	$0.50
Original insoluble soap recovery design, %	85	85	85	85	85	85	85	85	85	85
Cost of Tall Oil plant operation, $/tonne of tall oil	$50.00	$50.00	$50.00	$50.00	$50.00	$50.00	$50.00	$50.00	$50.00	$50.00
Soap content in weak BL, Kg soap/tonne of dry black liquor solids	29.3	29.3	29.3	29.3	29.3	29.3	29.3	29.3	29.3	29.3
Soap resin acid, %	37	37	37	37	37	37	37	37	37	37
Soap fatty acid, %	28	28	28	28	28	28	28	28	28	28
Tall Oil yield from soap, %	50	50	50	50	50	50	50	50	50	50
Tall oil value as fuel, $/tonne (38 GJ/tonne)	$342.00	$342.00	$342.00	$342.00	$266.00	$342.00	$418.00	$342.00	$342.00	$342.00
OUTPUT										
Current FA/RA ratio	0.72	0.72	0.72	0.72	0.72	0.72	0.72	0.72	0.72	0.72
Soap available now, tonnes per day	54.3	54.3	54.3	54.3	54.3	54.3	54.3	54.3	54.3	54.3
Soap available now, tonnes per day as CTO	27.1	27.1	27.1	27.1	27.1	27.1	27.1	27.1	27.1	27.1
Resin acids, tonnes per day	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Fatty Acids, tonnes per day	7.6	7.6	7.6	7.6	7.6	7.6	7.6	7.6	7.6	7.6
Fatty Acid required to increase FA/RA ratio, tonnes per day	2.44	4.45	7.46	9.97	4.45	4.45	4.45	4.45	4.45	4.45
Costs of purchased Fatty acids	$1,720	$3,133	$5,254	$7,021	$3,133	$3,133	$3,133	$2,938	$3,917	$4,896
Soap solubility minimum, kg/tDBLS	10	6	6	6	6	6	6	6	6	6
New Soap Production, tonnes per day	58.01	61.07	65.67	69.50	61.07	61.07	61.07	61.07	61.07	61.07

Total soap now available, Kg/tDBLS	31.3	33.0	35.4	37.5	33.0	33.0	33.0	33.0	33.0	33.0
Soap recovery, Kg/tDBLS	18.1	22.9	25.0	26.8	22.9	22.9	22.9	22.9	22.9	22.9
Soap recovery, tonnes per day	33.6	42.5	46.4	49.6	42.5	42.5	42.5	42.5	42.5	42.5
Tall Oil production, tonnes per day	16.8	21.2	23.2	24.8	21.2	21.2	21.2	21.2	21.2	21.2
Value of tall oil as kiln fuel	$5,739	$7,261	$7,930	$8,487	$5,648	$7,261	$8,875	$7,261	$7,261	$7,261
Cost of converting soap to tall oil, $/day	$839	$1,062	$1,159	$1,241	$1,062	$1,062	$1,062	$1,062	$1,062	$1,062
Net Value of Tall Oil, $/day	$3,180	$3,066	$1,516	$225	$1,453	$3,066	$4,680	$3,262	$2,283	$1,304
Net Value of Tall Oil, $/tonne	$190	$144	$65	$9	$68	$144	$220	$154	$108	$61
Net Value of Tall Oil as Fuel, $/year (350 d/yr basis)	$1,113,053	$1,073,219	$530,689	$78,580	$508,451	$1,073,219	$1,637,988	$1,141,762	$799,049	$456,336
Sulphuric Acid Solids returned to Recovery Cycle (tonnes/day)	2.1	2.7	2.9	3.2	2.7	2.7	2.7	2.7	2.7	2.7
Reduction in Solids to Recovery Boiler (tonnes / day)	14.6	18.5	20.2	21.7	18.5	18.5	18.5	18.5	18.5	18.5
% Reduction in Recovery Boiler Solids	0.79%	1.00%	1.09%	1.17%	1.00%	1.00%	1.00%	1.00%	1.00%	1.00%
Incremental Increase in Final Production (ADMT / day)	6.8	8.6	9.3	10.0	8.6	8.6	8.6	8.6	8.6	8.6
Value of Incremental Pulp Production (at $300/t and 350 days)	$709,899	$898,257	$980,939	$1,049,842	$898,257	$898,257	$898,257	$898,257	$898,257	$898,257
Value of Tall Oil and Incremental Production	$1,822,952	$1,971,476	$1,511,629	$1,128,422	$1,406,707	$1,971,476	$2,536,245	$2,040,019	$1,697,306	$1,354,593
Reduction in green house gas emissions, t/y	11,472	14,515	15,851	16,965	14,515	14,515	14,515	14,515	14,515	14,515
Value of reduced GHG emissions at $15/t credit	$172,073	$217,729	$237,771	$254,472	$217,729	$217,729	$217,729	$217,729	$217,729	$217,729
Net Value of Tall Oil / Production / GHG Credit.	$1,995,026	$2,189,205	$1,749,400	$1,382,895	$1,624,437	$2,189,205	$2,753,974	$2,257,748	$1,915,035	$1,572,322

4. CONCLUSIONS

Lab tests showed that adding tall oil fatty acids or waste fatty acids from vegetable oil processing could decrease tall oil soap solubility and increase soap skimming efficiency in the mills pulping a large percentage of grey-stage beetle-infested wood.

Full-scale mill trials were run over four days. Adding fatty acids increased tall oil soap skimming efficiency from 50.2% in the baseline tests to 71.8% based on total soap available, and from 76.7% in the baseline tests to 87.5% based on insoluble soap only.

Soap solubility in the skimmer feed liquors before adding fatty acids averaged 11.4 kg/tDBLS, whereas in three daily composite feed liquor samples taken after fatty acid addition commenced, it averaged 8.8 kg/tBLS, confirming that fatty acids had the desired effect on soap solubility.

Four of the five skimmed liquor samples taken before fatty acid addition had soap concentrations lower than the laboratory-measured solubility limit. Similarly, 13 of the 14 skimmed black liquor samples taken after fatty acid addition commenced had soap concentrations lower than the laboratory-measured solubility limit. For this reason, we assumed a soap solubility limit of 5 kg/tDBLS during the baseline tests, and 3.5 kg/tDBLS after starting fatty acid addition.

Samples of the soap skimmed after the trials appeared to be a blend of that collected before and during the fatty acid addition trials. Skimmed soap had acid numbers ranging from 128.6–131.4, with FA/RA ratios between 1.08–1.23. The acid number and FA/RA ratio were higher than those for soap collected immediately prior to starting fatty acid addition (acid number 120; FA/RA 0.7).

Tall oil soap transferred from the skimmer after the fatty acid addition trials was processed in the tall oil plant at Mill E without requiring any tall oil separation aids. About 165 tonnes of tall oil were produced when the soap skimmed over the four days prior to the trial, and the soap skimmed over the four-day-long trial was acidulated. Tall oil production was thus slightly over 20 tonnes per day for the whole eight days that the skimmer was in operation.

Acid numbers of the product tall oil as analysed at the mill ranged from 122.4–128.5 (assuming 2% moisture), which was in line with the results from laboratory acidulations of the skimmed soap. The FA/RA ratios in the product tall oil ranged from 0.96–1.24, which were also in line with our laboratory soap acidulation test results.

Economic analyses indicated that waste fatty acid addition could be economical at FA/RA ratios of up to 1.75, even when the value of burning the recovered tall oil in the mill's lime kiln was all that was considered, if natural gas and oil prices were high (>$9 Canadian/GJ). Depending on natural gas and fatty acid costs and the required FA/RA ratio for good soap skimming, net profits of $1.4 to $2.8 million per year were estimated when all the potential benefits of improved tall oil soap recovery were considered.

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